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# Dolomitization processes in hydrocarbon reservoirs: insight from geothermometry using clumped isotopes

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**Abstract**

Clumped isotopes geothermometry was applied to two dolomitic hydrocarbon reservoirs. Results indicate that late burial dolomitization occurred at ~110°C in the Albian Pinda dolostone (offshore Angola) and ~90°C in the Mano-Meillon dolostone (Aquitaine Basin, France), and did not continue on during subsequent burial/thermal evolution to present-day conditions (150-160°C). This study illustrates the great potential of the clumped isotopes approach to help unravel dolomitization processes in hydrocarbon reservoirs.


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*Keywords:* dolomite; clumped isotopes; temperature

## 1. Introduction

Many hydrocarbon reservoirs are found in dolomitized limestone and dolostone. Dolomitization can take place at various stages in the reservoir history, including syndepositional (evaporative and reflux dolomitization), eogenetic diagenesis (mixing zone and Coorong dolomitization), mesogenetic diagenesis (burial dolomitization) and tectonic-related events (telogenetic and hydrothermal dolomitization). It is generally considered that low temperature dolomitization often enhances reservoir properties while late, high temperature dolomitization does not, but there are exceptions to this rule of thumb. In conventional studies of dolomitic reservoirs it is sometimes difficult to unravel the nature of the dolomitization process, in particular when several dolomitization episodes were superimposed. Traditionally, investigators call upon tools such as fluid inclusion microthermometry and stable/radiogenic isotopes (O, C, Sr) in order to constrain conditions of dolomitization. These approaches have limitations, such as resetting of


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fluid inclusion Th temperatures during subsequent burial and equivocal interpretation of isotopic results that can lead to erroneous interpretation of the dolomitization processes involved.

In the recent years, a novel geothermometer[1] referred to as "clumped isotope paleothermometry" has been developed for application to carbonates. Clumped isotopes refer to the preferred molecular clumping of heavy isotopes ($^{13}C$, $^{18}O$) in the $CO_2$ molecule (compared to heavy-light or light-light isotopes) due to the greater thermodynamic stability of heavy bonds. Theory predicts that the abundance in clumped (heavy-heavy) isotopes in a compound should obey a stochastic (random) distribution. It was shown that deviation from the stochastic distribution is representative of the carbonate formation temperature and independent of its bulk isotopic composition. This temperature-dependence property of clumped isotopes (less abundant as temperature increase) offers the possibility to use them as a quantitative paleothermometer. Paleothermometry based on clumped isotopes in carbonates uses the so-called Δ47 parameter (mass 47), which is measured by IRMS after acid digestion of the carbonate under controlled conditions. In practise, the lower the carbonate Δ47 value, the greater the formation temperature.

So far, clumped isotope thermometry has mostly been applied to (near-)surface environments, paleo-climatology and low-temperature diagenesis[2]. Very few studies have dealt with deeply buried carbonate reservoirs, due to because the limited calibration range for the thermo-dependence of clumped (<100°C). However, recently this calibration[3] was extended up to 250°C, thereby offering the possibility to investigate carbonates imprinted by deep burial diagenesis.

In the present study, the objective was to explore the use of clumped isotopes thermometry for the understanding of massive dolomitization in two well-known dolomitic hydrocarbon reservoirs, i.e. the Pinda Formation (Albian) in offshore Angola and the Mano-Meillon Formations (Upper Jurassic) in the Aquitaine Basin, France. The results illustrate the usefulness of the approach, and provide new insights regarding the dolomitization models previously established for the two formations.

## 2. Methods and samples

All clumped isotope measurements, i.e. Δ47 determinations, were performed at the isotope laboratory facilities of the Carbonate research Group at Imperial College, London. The procedure involves: 1) chemical/physical pretreatment of the samples to remove organics (crushing, $H_2O_2$, plasma asher…); 2) acid digestion at 90°C; 3) purification of liberated $CO_2$ in a gas vacuum line; and 4) measurement of isotopic ratios on a modified dual inlet Thermo Fisher MAT253 mass spectrometer (measuring masses 44, 45, 46, 47, 48, 49). Measurements are made against a calibrated reference gas (Oztech), and corrected for "non-linearity" effects (quantified by establishing the relationship between Δ47 and δ47 for a series of heated gases). Final Δ47 values are expressed relative to URF[4]. Clumped isotope temperatures are then calculated using the Δ47-temperature calibration[3].

All samples investigated in this study are bulk carbonate samples. They were selected on the basis of their petrographical and mineralogical homogeneity, and are expected to be representative of single massive dolomitization events. Some samples may contain more than one generation of diagenetic carbonates, due to replacement (neomorphism) or overgrowth (cementation) processes which could not be resolved petrographically. However, the generation of interest is always largely dominant volumetrically over others. A total of 18 samples coming from 18 different cored wells (7 wells for the Pinda Formation, 11 wells for the Mano Formation) were studied.

## 3. Pinda dolomite Formation, offshore Angola

The Pinda dolomite Formation (Albian) constitutes a major hydrocarbon reservoir in the Lower Congo basin, northern offshore Angola. It is composed of pervasively dolomitized shallow-marine, oolithic-pisolitic platform carbonates lying at present-day burial depths between 2 and 3.5 km. The Pinda dolomite was interpreted[5] as being mainly early diagenetic (synsedimentary), although fluid inclusions and stable isotopes suggest late burial dolomitization at >100°C. The progressive decrease of $\delta^{18}O$ and increase of fluid inclusion Th values (similar to well temperatures) with depth was considered to reflect resetting in relation with continuous dolomitization by neomorphism during subsequent burial/thermal evolution.

Temperatures derived from clumped isotopes thermometry in this study are significantly lower, by 30-50°C, than fluid inclusion and present-day temperatures recorded at any given depth. -They range from 65 to 122°C, and cluster at about 110±10°C in samples from the deepest portion of the studied section, i.e. between 2.8 and 3.7 km depth.

The data suggest that massive burial dolomitization (neomorphism of the early dolomite) occurred at around 110°C and did not continue on to present-day burial temperature (~150°C). The reconstructed $\delta^{18}O$ value of the dolomitization water is between 4 and 6‰ PDT, in good agreement with the $\delta^{18}O$ value of 5 ‰ measured for present-day formation water in a nearby well.

## 4. Mano and Meillon dolomite Formations, Aquitaine basin, France

The Mano & Meillon dolomites (Upper Jurassic) are important gas reservoirs in the southern part of the Aquitaine basin, North of the Pyrenees, France. Both formations are interpreted as shallow marine, internal platform carbonate deposits that originated as limestone and were massively dolomitized during early and late diagenesis[6]. However the exact conditions of dolomitization are not well known. The two formations are found at very variable present-day depths in different sub-basins, ranging from <1 km to ~6 km. Although some areas suffered recent uplift, present-day depth represent maximum burial depth within 500 m or so. Because the dolomite could be sampled over a wide range of burial depths/temperatures (1-6 km, 50-160°C), this site offered a unique possibility to investigate the thermal history recorded by the clumped isotope signal in the absence of fluid inclusion data. In particular, it was interesting to explore whether burial dolomitization was a progressive or punctuated process. Analyzed samples are from two different depositional facies, i.e. grainstone and mudstone. The two shallowest samples (1-2km) are composed of limestone, whereas the others (2-6 km) are of dolostone.

The clumped isotope temperature recorded in the two shallow limestone samples is similar to present-day well temperature, i.e. ~45-50°C. In contrast, clumped isotope temperature recorded in the dolostone reservoir at depths below 2 km is systematically lower than present-day temperature by 20-70°C (with one exception at 5.4 km). There is no difference between grainstone and mudstone records in the two formations. The clumped isotope temperature for the deepest samples (i.e., between 3.5 and 5.5 km) tend to cluster around 90±10°C. The exception at 5.4 km exhibits a singular coarsely crystalline texture which may reflect local recrystallization by some hydrothermal (?) fluids.

In spite of some scatter in the data, the results suggest a major burial dolomitization event at ~90°C in the two dolomite formations investigated. They also suggest, in agreement with the Pinda Formation results (see above), that dolomitization did not continue during subsequent burial which brought the studied reservoirs to temperatures up to 160°C.

## 5. Conclusions

Application of the clumped isotopes thermometry method to two major dolomitic reservoirs permitted to constrain the temperature of late burial dolomitization. The later occurred at ~110°C in the Albian Pinda dolomite in offshore Angola, and at ~90°C in the Mano-Meillon Formations in the Aquitaine Basin, France. These dolomitization temperatures are significantly lower (by 40-60°C) than present-day temperature (up to 160°C). This study illustrates the great potential of the clumped isotopes approach to help unravel dolomitization processes that generated hydrocarbon reservoirs.

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## References

1. Eiler J. M. & Schauble E. 18O13C16O in Earth's atmosphere. *Geochimica et Cosmochimica Acta*, 2004, 68, 4767-4777.
2. Dale A., John C. M., Mozley P. S., Smalley P. C. & Muggeridge A. H. Time-capsule concretions: Unlocking burial diagenetic processes in the Mancos Shale using carbonate clumped isotopes. *Earth and Planetary Science Letters*, 2014, 394, 30-37.
3. Kluge T., John C. M., Jourdan A. L., Davis S. & Crawshaw J. Laboratory calibration of the calcium carbonate clumped isotope thermometer in the 25-250°C temperature range. *Geochimica et Cosmochimica Acta*, 2015, in Press.
4. Dennis K. J., Affek H. P., Passey B. H., Schrag D. P. & Eiler J. M. Defining an absolute reference frame for 'clumped' isotope studies of CO2. *Geochim. Cosmochim. Acta*, 2010, 75, 7117-7131.
5. Eichenseer H. T., Walgenwitz F. R. & Biondi P. J. Stratigraphic control on facies and diagenesis of dolomitized oolitic siliciclastic ramp sequences (Pinda group, Albian, offshore Angola). *Aapg Bulletin-American Association of Petroleum Geologists*, 1999, 83, 1729-1758.
6. Barnett A., Pernin C. and Virgone A. Quick look sédimentologique et évaluation réservoir de la dolomie de Mano (Meillon) - France. Tech. rep., TOTAL E&P.. DGEP/GSR/TG/ISS R05-105. 2006.